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13. ABSTRACT (Maximum 200 words)

In line with proposal objectives three parallel and connected thrusts were pursued: 1) investigation of the use of Langmuir-Blodgett (LB) films in MIS Schottky structures to modify the barrier properties of junctions made from SiO₂/Si and GaAs(100), 2) the treatment of Si and GaAs(100) surfaces with inorganic P and S compounds in order to favorably modify the electrical behavior, primarily via passivation of surface traps, and 3) the development of self-assembled monolayers of organothiols, in particular, alkanethiolates on GaAs(100) as a means to modify the electrical properties of the surface and more recently as

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a new class of ultrahigh resolution lithographic resists for nanofabrication. In support of each of these thrusts extensive work was carried out in two areas: **characterization of the structure and composition of the surface films**, primarily by infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and ellipsometry and **characterization of the electrical behavior of the film and its interface with the semiconductor**, primarily by fabrication of MIS Schottky diode structures and measurement of I-V and C-V response, but also including limited photoluminescence and photoreflectance measurements. All the work was directed ultimately for the chemically bonded molecular film samples. The LB films represented molecules adsorbed with no chemical bonding, the inorganic treatments represented chemically modified surfaces with molecular groups and the chemically bound inorganic films contained both the previous aspects.

FINAL REPORT

1. ARO PROPOSAL NUMBER: 27770-CH
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 - 1) C.W. Sheen; finished requirements for a PhD in Polymer Science in December, 1992.
 - 2) J. Shi; finished requirements for a MS in Chemistry, Summer, 1992. She received partial support from this project during her training.
 - 3) O.S. Nakagawa, PhD student in Engineering. He received partial support from this project during his training. He finished his PhD thesis in Electrical Engineering in May 1993.

8. Summary of Project Results

The overall objective of the initial proposal was to explore the feasibility of altering and controlling semiconductor surface and interfacial traps by chemically binding organic molecular groups to the semiconductor surface. The intent was to focus on the III-V compounds, primarily GaAs and to a lesser extent on Si, and apply known chemistry involving the constituent elements of the semiconductor and organic functional groups to the development of methods for forming robust chemical bonds at the semiconductor surface. Further, the motivation was on developing chemical methods coupled with electrical and other measurements on simple device structures as opposed to an emphasis on development of devices.

In line with these objectives three parallel and connected thrusts were pursued: 1) investigation of the use of **Langmuir-Blodgett (LB) films** in MIS Schottky structures to modify the barrier properties of junctions made from SiO_2/Si and $\text{GaAs}(100)$, 2) the treatment of Si and $\text{GaAs}(100)$ surfaces with **inorganic P and S compounds** in order to favorably modify the electrical behavior, primarily via passivation of surface traps, and 3) the development of self-assembled monolayers of **organothiols**, in particular, alkanethiolates on $\text{GaAs}(100)$ as a means to modify the electrical properties of the surface and more recently as a new class of ultrahigh resolution lithographic resists for nanofabrication. In support of each of these thrusts extensive work was carried out in two areas: **characterization of the structure and composition of the surface films**, primarily by infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and ellipsometry and **characterization of the electrical behavior of the film and its interface with the semiconductor**, primarily by fabrication of MIS Schottky diode structures and measurement of I-V and C-V response, but also including limited photoluminescence and photoreflectance measurements. All the work was directed ultimately for the chemically bonded molecular film samples. The LB films represented molecules adsorbed with no chemical bonding, the inorganic treatments represented chemically modified surfaces with molecular groups and the chemically bound inorganic films contained both the previous aspects.

(a) Langmuir-Blodgett Films

In the early phase of the program, we set out to perform chemical modification of GaAs and Si surfaces by Langmuir-Blodgett (L-B) as well as self-assembled films and evaluate the alteration of the electrical interface using Schottky barrier electrical measurements. These studies enabled us to establish baselines for evaluating the effects of chemical modification on the surface electrical barrier, and due to the extreme sensitivity of carrier transport across the metal-semiconductor (MS) contact to the interfacial barrier, the current-voltage (I-V) characteristics also help assess film integrity.

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Cadmium Arachidate [$\text{Cd}(\text{C}_{19}\text{H}_{39}\text{CO}_2)_2$ or $\text{Cd}(\text{Ar})_2$ films. Overall, our results indicated that excellent device interfaces were formed with the Cd salts. The I-V plots revealed an increase in Schottky barrier height for n-GaAs and a reduction for p-GaAs. This is consistent with a negative interfacial charge induced by the Cd salt film. The diode ideality factor shows negligible change, suggesting that the applied voltage drop across the interfacial layer is negligible. These results showed that pinhole-free films were formed by our processing.

In order to evaluate some earlier promising results reported in the literature on the removal of organics from $\text{Cd}(\text{Ar})_2$ films, we exposed samples to UV-ozone treatment, but this resulted in considerable native oxide growth, causing the devices to lose Schottky-like rectification properties. Even with much shorter ozone treatment periods, we found that the plasma ashing procedure reported in the literature for leaving behind a monolayer of metallic Cd on the semiconductor surface¹ adds a native oxide of considerable thickness; our finding then suggests that it is this native oxide rather than Cd atoms at the surface that alters the Schottky barrier properties. Consequently this application of LB films was evaluated as not particularly useful.

In view of the well-known sulfur passivation of the GaAs surface, we also attempted to modify the chemistry of the film with exposure to H_2S prior to metallization. Our results suggest different behaviors on n- and p-GaAs: On the n-type samples, the I-V characteristics revert to those of the control (MS contact with no film), while no such behavior is seen for p-GaAs. It appears that the sulfurization of the arachidate film may introduce deep levels at the GaAs surface causing different charges in n- and p-GaAs. The C-V characteristics do not display significant differences between the control and modified diodes. It was seen that no particular advantage to barrier modification was gained by this experiment.

We also carried out the first systematic study of odd- and even-layers of cadmium arachidate LB films on Si, both n- and p-type. Apart from the expected gradual evolution of the Schottky-type electrical characteristics towards those of MIS capacitive structures, the MIS Schottky *diode* with an LB monolayer had significantly higher leakage than the one with two monolayers, evidently due to the differences in the time of immersion in buffered water solution.

Polyimide Films. Y-type bilayers of polyimide films were deposited by L-B on both GaAs and Si, followed by overnight curing in a 3:1:1 benzene/pyridine/acetic anhydride solution. On n-GaAs where both the control and modified devices are rectifying, a slight increase in barrier height is seen, but with a significant increase in *n*-factor. On p-GaAs, the MS contact becomes more ohmic with the polyimide layer, again indicating a barrier decrease. These results tend to suggest the interfacial charge introduced by the polyimide layer is rather small, and that the device behavior is primarily altered by the thin, tunnelable polyimide layer. Noticeably different behavior is seen on Si, with the Au/n-Si contact becoming leaky with the polyimide film, and the Au/p-Si contact turning *less* ohmic. The LB studies did not reveal evidence of any particular advantages to Schottky barrier modification on both Si and GaAs, and so further efforts were channeled into the following more prospective areas.

(b) Phosphorous Pentasulfide Treatment of GaAs

As a parallel and complementary effort to the formation of organic films with molecular groups (see below), interface modification by simple inorganic compounds and species comprised of the active atoms in the organic functional groups were investigated, in particular S but also P. Since a few literature reports claimed that these types of inorganic elements exhibit beneficial passivating effects, it was important to follow up previous studies both to look for improvements and to help direct the organic film work. A Schottky barrier study was carried out in which the passivation effects of solution treatment by P_2S_5 and the well known ammonium sulfide solution treatment were compared. Both these treatments give rise

to an increased dependence of the Schottky barrier height on the metal work function. We also pursued degradation studies of the various surface treated GaAs Schottky barriers. These results contrast to those of Na_2S -treated GaAs Schottky diodes, where no Schottky barrier modification is seen. However, it is interesting to note that all these three types of S-treatment give rise to PL enhancement, while evidently their influence on the MS electrical interface is different. XPS analysis showed that the surface films contained P, S and O with the latter presumably associated with a surface phosphate type of layer. These data could be understood in terms of a multilayer coating of P_2S_5 which formed S bonds to the GaAs and oxidized slowly on the top to form PO_x species. From our results we can conclude that the GaAs surface passivation effects of P_2S_5 are virtually identical to those of $(\text{NH}_4)_2\text{S}$, from the viewpoint of PL and as well as Schottky barrier heights. The stronger As-disulfide bonds at the P_2S_5 -treated GaAs surface may also contribute to better stability of the metal/GaAs interface.

In an offshoot of our surface modification studies, we have developed a new technique for p-n junction and ohmic contact formation in Si using phosphorous vapor exposure, and (with a protective SiO_x overlayer) rapid thermal annealing to drive in the phosphorous. This simple fabrication process offers low thermal budget and is an alternative for shallow junction formation both in Si microelectronics and in low-cost Si solar cells fabricated on polycrystalline Si.

(c) Alkanethiolate Self-Assembled Monolayers (SAM) on GaAs

In line with the original proposal to try to react organothiols with cleaned GaAs(100) surfaces, an extensive number of experiments were carried out using a variety of conditions in which the semiconductor was exposed to n-octanethiol ($\text{C}_{18}\text{H}_{37}\text{SH}$)

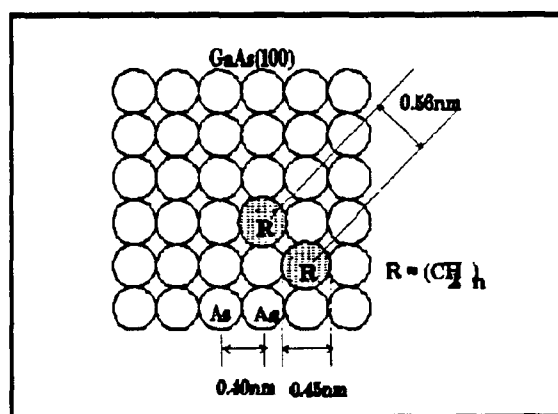


Figure 1

and related derivatives. Within a year it was discovered that exposure, under argon atmosphere, to molten thiol at $\approx 100^\circ\text{C}$ leads to the formation of single monolayer films, a finding which validated our original concepts that such films could be formed using appropriate chemistry. Over the course of the next year efforts were made to characterize: 1) the molecular structure and chemical nature of a series of films using different alkane thiols, of general structure $\text{X}(\text{CH}_2)_n\text{SH}$, with $n = 9-23$ and $\text{X} = \text{CH}_3$, except for a limited number of experiments with $\text{X} = \text{CO}_2\text{H}$ and 2) the electrical properties, primarily through an extensive series of measurements on (conducting MIS) Schottky structures with a number of metals in order to delineate surface passivation that should show up as an increase the sensitivity of the junction barrier to the metal work function. This work was augmented with photoluminescence and photoreflectance measurements. By the use of a combination of ellipsometry, IRS, XPS and wetting measurements it was concluded that the films are one monolayer thick (≈ 1.5 nm for $n = 17$), exhibit an average stoichiometry of one molecule per every two As atoms as calculated for a perfect (100) surface layer of As, exhibit direct bonding of the S atoms to As with less than a percent or two of oxide present when the films are carefully made and possess highly hydrophobic (water repellant) and oleophobic (oil repellant) surfaces. IRS showed that for the longer molecules, $n = 15-17$, the chains are approximated by extended rods with tilts from the surface normal of $55-60^\circ$, whereas for the short molecules the chains become somewhat conformationally disordered. The molecule/As stoichiometry together with the other evidence suggests that the films are translationally ordered with a $c(2 \times 2)$ overlayer structure on the (100) surface. A simple schematic of this structure is shown in Figure 1 where it can be seen that the 0.45 nm diameter of the extended $-(\text{CH}_2)-$ chain precludes occupation of adjacent As atoms, spaced at 0.40 nm, forcing the occupation of next nearest As atoms in the $c(2 \times 2)$ structure. The figure shows the chains vertically extended from the surface for simplicity; however, in reality the chains are tilted $\approx 55-60^\circ$ in order to maximize intermolecular interactions.

This work was unprecedented in that it was the first discovery of a new class of self-

assembled monolayers which involve direct bonding to a bare semiconductor surface. In actuality only a few types of self-assembled monolayers have been reported and this new class is a major contribution to this field of surface chemistry. However, this appears not to be the only significant discovery in this work. As an ongoing extension of the structural analysis, high resolution XPS studies are being conducted in collaboration with Ulrik Gelius at Uppsala University in Sweden. These results are now showing the presence of hydride species in the alkanethiolate monolayer, presumably at the alternate As atoms in the $c(2 \times 2)$ structure. However, it is also becoming apparent from these studies that the bare GaAs surface, when prepared by stripping an epi overlayer of AlGaAs, is covered with As-H species, an apparently remarkable finding with significance in the field of semiconductor processing, reminiscent of the Si-H discovery in HF treatment of Si surfaces.² Another promising outcome of this work is the discovery that the $C_{18}H_{37}S$ -based film possesses a sufficiently efficient combination of sensitivity toward electron beam degradation and resistance to chemical etch solutions that it appears to be an excellent candidate for an ultrahigh resolution positive resist for lithographic applications.

In parallel with these studies, the electronic properties of the thiol film/GaAs interface were studied by measuring the I-V and C-V characteristics of Schottky barriers formed by thermal evaporation of metals (Au, Pd, Ni, Cu, Cr, Ag, Ti, Al, In and Mg) with very different work functions (and chemical reactivity with GaAs), onto film-covered n-GaAs surfaces. These results yield the very important conclusion that the electrical interface is of *very high quality*. This is shown by the fact that highly reproducible Schottky diodes were obtained with near-unity ideality factors and very good matching of Schottky barrier heights determined from current-voltage (I-V) and capacitance-voltage (C-V) measurements. The latter behavior is in contrast to that of an oxidized interface and so is consistent with the XPS observation that the presence of thiol inhibits the formation of a native oxide on GaAs. It was found that both enhancement and reduction of the barrier height occur, depending on the metal. In general, the barrier height, with the octadecyl-thiol SAM modification, tends to move towards

the Schottky limit, i.e., diodes with low work-function metal tend to show Schottky barrier height reduction while those with high work function metals display barrier enhancement. This trend **implies *partial* reduction of the GaAs surface state density**. Since it is known that the Schottky barrier height of a metal-semiconductor interface is also affected by metal-semiconductor chemical reaction and interdiffusion, it is possible that these latter effects are also partly affected by the SAM treatment. We have also studied the Schottky barrier properties as a function of the number of C atoms in the alkane thiol self-assembled monolayer. A linear relationship has been obtained between the number of C atoms and the barrier height, which agrees with the structural characterization result that **the films are very uniformly formed with discrete thicknesses according to molecular size**. This type of fine control of a *non-oxidized* GaAs interface appears to be unique.

In addition to Schottky barrier formation, we also carried out photoreflectance (PR) measurement, to determine the surface band bending change *without any metal* deposition. These data confirm modification of the GaAs surface barrier by the octadecyl thiol. We also performed a very limited set of photoluminescence (PL) measurements (in collaboration with Claude Sandroff at Bellcore) using a SAM/GaAs/AlGaAs double heterostructure, but failed to see any photoluminescence enhancement which would indicate a reduction in the surface recombination velocity for excess carriers in the semiconductors. This is in contrast to the results reported for $(\text{NH}_4)_2\text{S}$, P_2S_5 and small thiol molecules (less than 6 carbons). It is not clear why this difference in behavior exists but it could be due to the continued existence of a small population of surface traps remaining at the organic film interface because of the inability of the larger organic molecules to totally cover the surface sites in comparison to the small inorganic S type species. However, since improvements in the perfection of the organic film still seem quite possible, some enhancement of the *surface* recombination lifetime accordingly might still be on the horizon. Also protecting the monolayer-covered surface with a low-temperature-deposited dielectric film could help assist the process.

Publications and Graduate Theses resulting from the Program

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